JOURNAL OF MATERIALS SCIENCE 38 (2003) 3013–3017

Effect of valve regulated lead/acid battery positive paste carbon fibre additive

R. J. BALL*
Department of Engineering and Applied Science, University of Bath, Bath, BA2 7AY, UK
E-mail: richard.ball@bristol.ac.uk

R. EVANS, E. L. THACKER
Enersys Newport, Stephenson Street, Newport, South Wales, NP19 0XJ

R. STEVENS
Department of Engineering and Applied Science, University of Bath, Bath, BA2 7AY, UK

The majority of lead acid battery failures can be attributed to degradation of the positive active material. In this paper the results from a study to investigate the effects of adding carbon fibre additive to red lead positive paste are presented. The test batteries manufactured were evaluated using capacity and cycle life tests prior to destructive examination and analysis using scanning electron microscopy and X-ray diffraction. Results suggest the addition of carbon fibre to positive paste increases capacity by approximately 20%. Significant improvements in cycle life were also observed.

1. Introduction

Valve regulated lead acid (VRLA) batteries have been on the market for several decades [1]. Recent advances in technology and environmental issues have resulted in an increasing demand for VRLA batteries in a range of applications, including Uninterruptible Power Supplies (UPS), Motive Powers [2, 3] and Starting, Lighting and Ignition (SLI) [4]. Batteries utilised in any of the above applications have a finite life due to deterioration of the various components of the battery during its operation.

Depending on the application and operational environment, battery failure can be a consequence of a range of processes involving the electrodes, electrolyte or ancillary components [5]. The most common cause of battery failure is reported to be premature capacity loss [6], which describes a reduction in performance ultimately resulting in the battery's failure.

This is generally a result of degradation of the positive active material (PAM). The addition of fibres to lead/acid battery PAM, to improve performance, has been reported previously. Synthetic fibres have been used to ensure sufficient strength of active materials by improving rigidity and durability of unformed plates. This reduces the risk of damage during handling [7]. Battery power characteristics can be improved by the addition of conductive fibres. These not only have the ability to enhance the mechanical properties of the electrode, but also the electrical properties. A number of different conductive fibres have been used in battery pastes such as carbon and tin coated glass [8]. Carbon fibres have good mechanical properties compared to lead oxide, a low density, are electrically conductive, and have reasonable stability in sulphuric acid electrolyte environments. This paper describes work carried out to determine the effects of adding short lengths (a few millimetres) of carbon fibres to VRLA battery positive paste. It was envisaged that these additives would improve mechanical properties and electrical conductivity of the formed PAM, thus enhancing battery performance.

A small quantity (0.25 wt%) of carbon fibres was added to standard red lead-based positive paste. The resulting monobloc showed an increase in capacity of approximately 20%. The paste was removed from the grid and ground for X-ray diffraction (XRD) analysis. Scanning electron microscopy (SEM) images of dry paste compact fracture surfaces allowed carbon fibre positions within the pastes to be observed.

2. Experimental methods

2.1. Manufacture of test batteries

Batteries were constructed from a commercial SBS40 (Sealed Battery System, 40 Amp hour) flat plate design, used by Hawker Energy Products Ltd., Newport. A monobloc consists of 6 cells in series, each containing 19 interleaved electrodes, 9 positive and 10 negative. Electrodes were manufactured from a pure lead grid and separated with 100% glass microfibre separators manufactured by Hollingsworth and Vose.

Results from three different PAM types are compared in this paper. In addition to the experimental red lead paste containing carbon fibres, results from the study

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*Present Address: Interface Analysis Centre, University of Bristol, Oldbury House, 121 St Michael's Hill, Bristol, BS2 8BS

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TABLE I Raw materials used to manufacture positive paste

	Red lead (wt%)	Grey oxide (wt%)	Carbon (wt%)
Red lead (carbon)	99.75	0	0.25
Red lead	100	0	0
Grey oxide	10	90	0

TABLE II Performance of batteries manufactured with different positive pastes

Positive paste	Cycles to failure
Red lead (carbon)	124–129
Red lead	28
Grey oxide	120

of a pure red lead paste, and grey oxide based paste are also presented. PAN based high conductivity carbon fibres, of length several millimetres, were added to the red lead paste. The raw material compositions of these pastes are shown in Table I.

2.2. Electrical testing of batteries

A number of different electrical tests were carried out on the experimental batteries using Digitron cycling units. Capacity tests were performed at a C5 rate. This involved measuring the time taken for the battery to reach a voltage of 10.2 V under a load of 7.05 A. The time taken for this to occur should be a minimum of 5 h. High rate cycle life tests were conducted using a 33.6 A discharge in one minute and low rate discharge tests using a 6 A discharge in 3 h. A minimum of 2 batteries from each batch produced were subjected to electrical tests.

2.3. X-ray diffraction

Compositional analysis of the active materials was determined using X-ray diffractometry. Samples removed from batteries were rinsed with distilled water and subsequently dried before grinding into a fine powder. Grinding times were restricted to a maximum of 10 min. to keep the conversion of alpha to beta lead dioxide to a minimum. Powders were placed into a standard aluminium glass-slide-back sample holder. A Phillips 1830 diffractometer was used with Cu K_{α} radiation. Scans were conducted in the 2-theta range of 20 to 60°, with a scan time of 3 s per degree and step size of 0.005°. Phases were identified by comparison of patterns with standard data obtained from the Joint Committee for Power Diffraction Studies (JCPDS).

2.4. Scanning electron microscopy

Scanning electron microscopy was used to obtain images of active material fracture surfaces. Formed active material samples were prepared by glueing dried pieces to a planchette using conducting cement.

Samples were sputter coated with a thin layer of gold approximately 10 nm in thickness to reduce charging and improve image quality. Examination was carried out in a Camscan 3 scanning electron microscope using a working distance of 24 mm and an electron beam voltage of 20 kV.

3. Results and discussion

3.1. Electrical results

Capacity tests were carried out at the C5 rate for a standard battery. Initially the as received capacity indicated an improvement of only 10%, however, after a high rate discharge/charge conditioning cycle, the battery exceeded a 20% improvement in capacity.

Cycle life tests were carried out at both high and low rate discharges. The 20% improvement in capacity was maintained at the high discharge rate for at least 1000 cycles. Capacity was noted to decline gradually with increasing cycling, finally 'failing' at 50% of nominal capacity after approximately 10,000 cycles.

Low rate discharges maintained a relatively flat discharge profile with a capacity approximately 10% higher than standard batteries. Failure occurred rapidly between cycles 124 and 129. When a comparison is made between similar design batteries containing different PAMs a significant improvement in performance is observed in the battery with carbon fibre additive, Table II. The cycle life is comparable to that of a similar battery manufactured using a grey oxide based paste.

3.2. Phase analysis

A compositional analysis of the dried unformed pastes obtained using XRD is given in Table III. Dried unformed positive paste manufactured from red lead based paste consisted mainly of β-PbO (orthorhombic) and Pb_3O_4 (orthorhombic), but also contained a small proportion of α-PbO (tetragonal). Some sulphation had occurred with the formation of tribasic lead sulphate (3BS) and its hydrate. There was no evidence of tetrabasic lead sulphate (4BS) at this stage. In comparison the grey oxide based paste consisted mostly of α-PbO with a small amount of additional oxides and basic sulphates.

Table IV shows the composition of the cycled pastes. The batteries were cycled to failure and the composition of the PAM determined. Active materials were found to consist mainly of β-PbO_2 plus a small proportion of $PbSO_4$. Slightly more basic lead sulphates were identified in the red lead paste containing carbon

TABLE III Composition of dried unformed positive pastes

(%)	β-PbO	α-PbO	Pb_3O_4	3BS	3BS·H_2O	Other
Red lead (carbon)	46	10	30	5	9	–
Red lead	35.6	33.6	19.6	0.4	10.8	–
Grey oxide	2.8	77.3	2.4	1.5	7.4	8.6

TABLE IV Composition of cycled positive active materials

(%)	β-PbO_2	α-PbO_2	$PbSO_4$	Basic Sulphates
Red lead (carbon)	80	2	6	12
Red lead	90.6	1	5.3	3.1
Grey oxide	79.9	5.6	10.3	4.2

fibres. The grey oxide based paste contained significantly more lead sulphate and α-PbO_2 compared to the other pastes.

4. Effect of carbon fibre presence in positive active mass

From the results carbon fibre additions do not appear to have a detrimental effect on paste formation. Most of the paste transformed to β-PbO_2 and the overall level of $PbSO_4$, which may passivate the active material, was low. There was some evidence of monobasic lead sulphate (1BS), however, basic sulphate formation appears to favour 3BS and 4BS formation.

Fig. 1 shows the carbon fibres in an unformed paste. Dispersion and orientation problems are apparent as significant numbers of fibres congregating in the mix appear to be aligned in one direction. In other regions, there was little evidence of carbon fibres in the paste. This is a processing problem, which should be possible to overcome.

Fig. 2 shows a carbon fibre protruding from a cycled paste compact. The fibre appears to be embedded in a cavity, a feature typical of many of the carbon fibres observed in the sample. A small number of cavities were also observed which had the same structure but no visible carbon fibre.

The cavity walls are lined with well-defined large crystalline structures, in contrast to the surrounding media, which is considerably smaller and of a less definite morphology. The surrounding media has a porous structure with a range of pore sizes from the sub-micron range to approximately 5–10 μm. The cavities, however, are considerably larger, see Fig. 3, between 50 and 100 μm in diameter.

As previously mentioned, the introduction of carbon fibres into the positive paste resulted in a significant improvement in capacity. The SEM micrographs also show evidence of the formation of large cavities, Fig. 3, which appear to have been caused by the presence of carbon fibres. Fibre pullout is the most probable explanation for the absence of carbon fibres in some cavities. Previous research by Tokunaga has demonstrated the ability of anisotropic graphite particles within the PAM to cause an increase in porosity. This was attributed to an expansion of the graphite due to anodic oxidation. It is possible that a similar mechanism may be occurring with the carbon fibres [9].

The initial aim of the carbon fibre addition was to improve active mass utilisation by providing an improved electrical network within the paste. It is possible, however, that the fibres are also affecting the physical paste structure. It is well documented [10] that the positive active mass swells during charge and contracts during discharge. Intuition suggests that it is possible that the presence of the carbon fibres are helpful in maintaining open channels, large enough to allow acid access, during the charge/discharge cycle that would otherwise be lost due to material deposition. An increase in porosity caused by the presence of anisotropic graphite has been shown to increase the discharge performance. This is believed to be due to the increased amount of electrolyte retained within the pores [11].

The fibres may also undergo dimensional changes that are contributing to the pore network. Overall the combined effect of mechanical reinforcement and current distribution along the fibres would be expected to have a long term beneficial effect.

Alternatively, or possibly in addition, the fibres may well be contributing to the control of compression

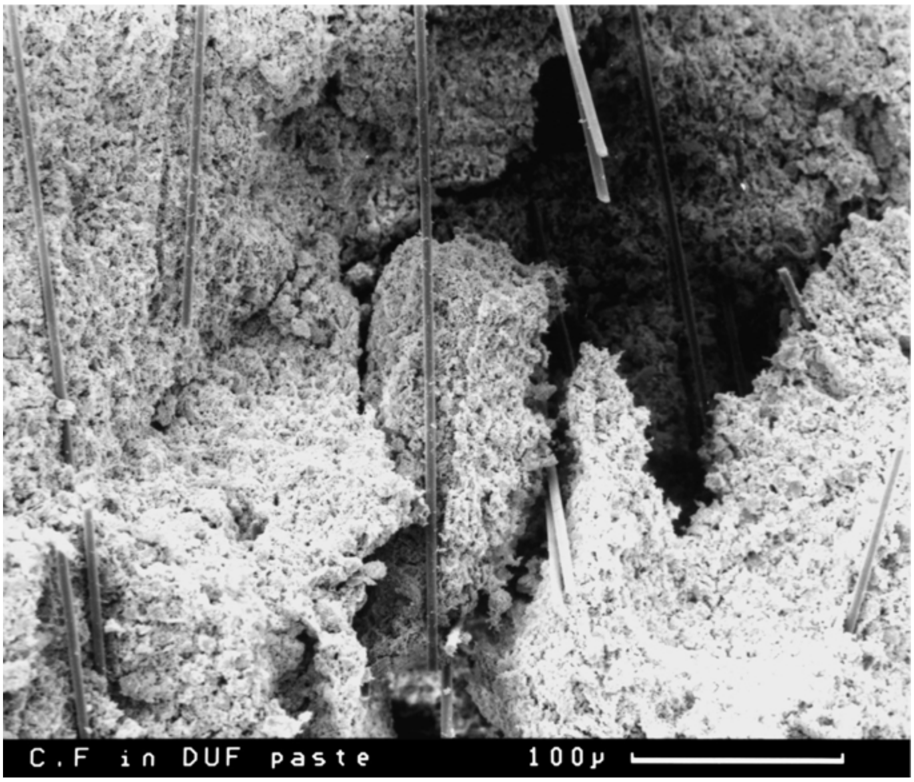

Figure 1 Dried unformed paste containing carbon fibres.

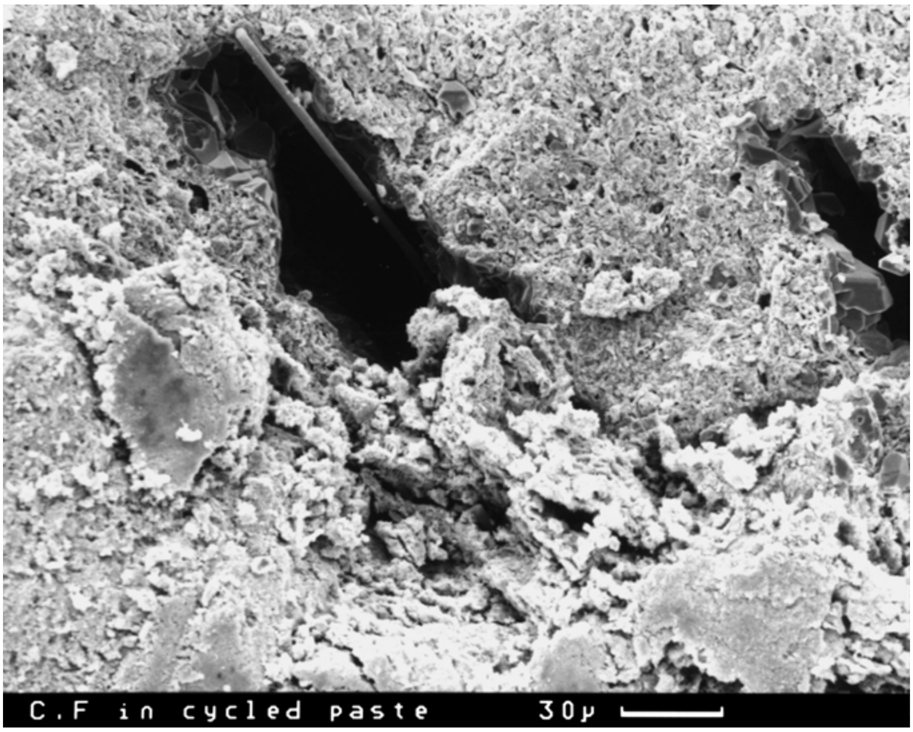

Figure 2 Carbon fibres evident in cycled pastes.

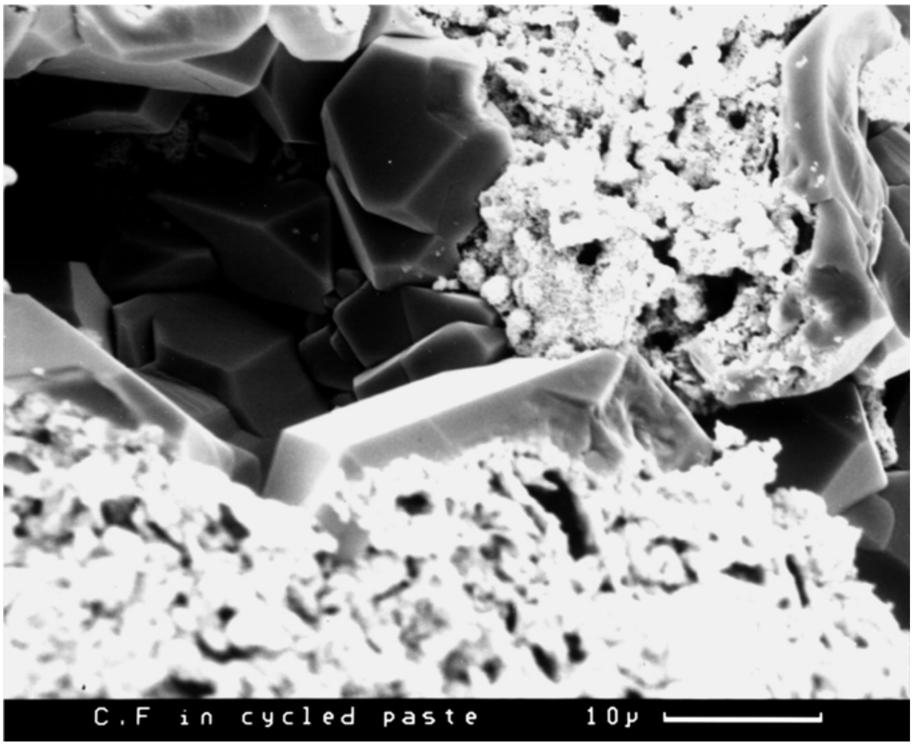

Figure 3 Formation of cavities accredited to presence of carbon fibres and the associated large polyhedral crystals.

levels, either by providing compression within the paste (if the fibres swell), or by providing a mechanically supporting network during discharge, thus helping prevent shedding of the active mass, which can lead to PCL.

5. Conclusions

The carbon fibres appear to remain stable in the battery during charge and discharge procedures. Improved capacity ratings of 10–20 %, especially at high rate charge/discharges, and significant increases in cycle life were observed on addition of 0.25 wt% chopped carbon fibres. The addition of carbon fibres to red lead based pastes appears to improve the performance. The manner in which the carbon fibres contribute to the improvements in performance is not yet clear, although is most likely to be due to the following factors working individually or together.

- Increase in mechanical integrity.
- Increase in porosity leading to greater acid access.

- Increase in electrical conductivity of the active material.

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*Received 24 December 2002
and accepted 30 April 2003*